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MOLECULAR ORBITAL THEORY OF THE LIGAND FIELD IN $[NiHal_4]^{2-}$ COMPLEXES

A. BOSE, R. RAI AND S. MITRA

DEPARTMENT OF MAGNETISM

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,
JADAVPUR, CALCUTTA-32.

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ABSTRACT An expression for magnetic susceptibility for $[NiHal_4]^{2-}$ complexes is deduced on the basis of the molecular orbital procedure of Stevens, Bose *et al.* and others, and compared with the experimental results on single crystals of $[Et_4N]_2[NiBr_4]$. An anisotropic reduction in spin-orbit coupling coefficient is found, which indicates an anisotropic overlap of ligand s- and p- charge clouds with the central d-charge clouds and also admixture of $3d^74p$ with $3d^8$ configurations. A sharper fall in the theoretical p^2f-T curve below 200 in contrast to the experimental curve and nearly 7% discrepancy between the two at the lowest temperature (100°*K*) suggest an appreciable change of the trigonal field coefficient Δ with temperature.

INTRODUCTION

In the tetrahedrally co-ordinated Ni^{2+} complexes the cubic ligand field energy pattern, into which the free ion ground level $3d^8\ ^3F$ is split up, consists of the levels $^3T_1$, $^3T_2$ and $^3A_2$, in increasing order of magnitude, which is just the reverse of the octahedral complexes, and the separation of the levels in the former case is 4/9 of the latter (Van Vleck, 1932; Gorter, 1932; Bleaney and Stevens, 1953). The X-ray studies by Peter Pauling (unpublished, reference by Gill *et al.*, 1959) of a series of isomorphous organometallic halides of Ni^{2+} e.g. $(Ph_3\ Me\ As)_2(NiHal_4)$ and $[(Et_4N)]_2 \cdot [(NiHal_4)]$ indicate that in all these salts the Ni^{2+} ion is tetrahedrally co-ordinated. This is supported by the optical absorption measurements in the latter salts (Gill *et al*, 1959; Goodgame *et al.*, 1961) which give bands round about 12500 cm^{-1}($^3T_1(F) \rightarrow\ ^3T_1(P)$) and 6900 cm^{-1}($^3T_1(F) \rightarrow\ ^3A_2(F)$) as against 25000 cm^{-1} ($^3A_2 \rightarrow\ ^3T_1(P)$) and 14000 cm^{-1}($^3A_2 \rightarrow\ ^3T_1(F)$) respectively, in the octahedral salts (Bose *et al.*, 1963). Also, the mean magnetic susceptibility measurements (Gill *et al*, 1959; Bose *et al.*, 1965) yield a high magnetic moment (about 3.6—4.0 Bohr magnetons) compared to the spin only value of 2.83, indicating the presence of large orbital contributions which is reasonable to expect if the $^3T_1$ triplet lies lowest in the Stark pattern.

X-ray measurements further indicate that the salts which form cubic crystal (space group $P2_1/3$) with four ions in the unit cell, $a = 15.5$ Å) have a trigonal distortion of the halogen tetrahedron round the Ni^{2+} ion, the trigonal axis passing

through one halogen at the vertex of the tetrahedron and the central Ni^{2+} ion, and normal to the base formed by the other three equivalent halogens. Thus the Ni^{2+} may be taken as under a small trigonal field superposed upon the predominant cubic field, so that a further splitting of the energy levels will occur and the $[(NiHal_4)]^{2-}$ complex will be magnetically anisotropic, the effect of which will be appreciable even in the mean susceptibility of the crystal (the crystal being cubic will not show magnetic anisotropy), in the higher order terms particularly at low temperature.

We have therefore derived a theoretical expression of the mean susceptibility of $(NiHal_4)^{2-}$—complexes on the basis of the molecular orbital theory of Van Vleck (1935), Stevens (1953), Bose *et al.* (1960) and compared it with the recent experimental values by one of the co-authors (S.M.) on $[(C_2H_5)_4N]_2NiBr_4$ the details of which will be published in a separate paper.

MOLECULAR ORBITAL THEORY OF TETRAHEDRAL Ni^{2+} COMPLEXES

In addition to the splitting of the ground state of Ni^{2+} ion by the tetrahedral field of the type T_d we have also to consider the effect of the excited ^3P state on $^3T_1(F)$ which arises from the same electron configuration. The lowest triplet $^3T_1(F)$ contains an admixture of ^3P, which itself remains unsplit under the said field and spans the same representation $^3T_1$ of the point group T_d.

A Ni^{2+} ion under a point group T_d can be treated as a system consisting of two *d*-holes, in which the three lowest states $^3T_1(F)$, $^3T_2(F)$ and $^3A_2(F)$ arise out of $(t_2)^2$, $(t_2)^1 \cdot (e)^1$ and $(e)^2$ configurations, respectively. Following the usual notations $t_a = \left| xy \right\rangle$, $t_b = \left| yz \right\rangle$, $t_c = \left| xz \right\rangle$ the determinantal wavefunctions of the lowest triplet $^3T_1(F)$ including the admixture of the ligand *s*- and *p*- orbitals with the central Ni^{2+} *d*-orbitals can be written as :

$$\begin{aligned} \psi_1 &= | \, t_c \, t_a \, | \\ \psi_2 &= | \, t_a \, t_b \, | \\ \psi_3 &= | \, t_b \, t_c \, | \end{aligned} \qquad \ldots \quad (1)$$

where ta, t_b and tc are single electron or hole orbitals in t_2 configuration. To include the effect of spon-orbit coupling, which takes the form $\Sigma(us)_i$ (Bose *et al.* 1960) we note that

$$\begin{aligned} \left\langle \psi_1 \right| u_{z_1} + u_{z_2} \left| \psi_2 \right\rangle &= \left\langle \psi_2 \right| u_{x_1} + u_{x_2} \left| \psi_3 \right\rangle \\ &= \left\langle \psi_3 \right| u_{y_1} + u_{y_2} \left| \psi_1 \right\rangle = i\zeta_i \end{aligned} \qquad \ldots \quad (2)$$

where ζ_i is the spin-orbit coupling coefficient modified by covalency overlap, a result similar to Stevens (1953) for single *d*-electron case. Here u_{r_1} and u_{r_2} are the *r*-th component of operator for hole number 1 and 2 respectively.

Further, the absence of a centre of inversion in these tetrahedral complexes introduces a feature which does not occur with octahedral, which is that $3d^7 4p$ configuration can be admixed with $3d^8$, the consequence of which may be considered to be that the holes are not in pure $3d$-orbits but in orbits which are an admixture of a $3d$- with a $4p$-wavefunction. Then following Bates *et al.* (1962), Bates (1963), Wolfsberg and Helmholz (1952) and taking this admixture the orbitals $|xy\rangle$, $|yz\rangle$ and $|xz\rangle$ used in (1) are finally written as :

$$t_a = |xy\rangle = N\left[\frac{1}{(1+\gamma^2)^{\frac{1}{2}}}\left\{dxy + \gamma|z\rangle\right\} + \frac{\lambda_1}{2}(\sigma_1+\sigma_4-\sigma_2-\sigma_3)\right.$$

$$\left. + \frac{\lambda_2}{2}\left\{\frac{1}{2}(\pi_{x_3}+\pi_{x_2}-\pi_{x_1}-\pi_{x_4}) + \frac{\sqrt{3}}{2}(\pi_{y_4}+\pi_{y_1}-\pi_{y_2}-\pi_{y_3})\right\}\right]$$

$$t_b = |yz\rangle = N\left[\frac{1}{(1+\gamma^2)^{\frac{1}{2}}}\left\{dyz+\gamma|x\rangle\right\} + \frac{\lambda_1}{2}(\sigma_1+\sigma_3-\sigma_2-\sigma_4)\right.$$

$$\left. + \frac{\lambda_2}{2}\left\{\frac{1}{2}(\pi_{x_4}+\pi_{x_2}-\pi_{x_1}-\pi_{x_3}) + \frac{\sqrt{3}}{2}(\pi_{y_4}+\pi_{y_2}-\pi_{y_1}-\pi_{y_3})\right\}\right]$$

$$t_c = |xz\rangle = N\left[\frac{1}{(1+\gamma^2)^{\frac{1}{2}}}\left\{d_{xz}+\gamma|y\rangle\right\} + \frac{\lambda_1}{2}(\sigma_1+\sigma_2-\sigma_3-\sigma_4)\right.$$

$$\left. + \frac{\lambda_2}{2}(\pi_{y_1}+\pi_{y_2}-\pi_{y_3}-\pi_{y_4})\right) \qquad \ldots (3)$$

in which N is the normalizing factor and λ's are measures of admixture of ligand s- and p-orbitals with the central $Ni^{2+}d$—orbitals; dxy etc., represent the major $3d$ contributions and $\gamma|z\rangle$ etc. the $3d^7\,4p$ contributions.

Taking the trigonal axis of the complex as the axis of quantization, the appropriate trigonal orbital states for lowest triplet are :

$$|+\rangle = -\frac{1}{\sqrt{3}}\left[\omega|\psi_1\rangle + \omega^2|\psi_2\rangle + |\psi_3\rangle\right]$$

$$|0\rangle = \frac{1}{\sqrt{3}}\left[|\psi_1\rangle + |\psi_2\rangle + |\psi_3\rangle\right] \qquad \ldots (4)$$

$$|-\rangle = \frac{1}{\sqrt{3}}\left[\omega^2|\psi_1\rangle + \omega|\psi_2\rangle + |\psi_3\rangle\right]$$

where $\omega = \exp\left(-\frac{2\pi i}{3}\right)$

so that inclusive of covalency the non-zero matrix elements of u_ξ, u_η, u_ζ are given by (ζ is the direction along the trigonal axis and with ξ and η form a right handed orthogonal system of coordinates).

$$\langle + | u_\zeta | + \rangle = -\langle - | u_\zeta | - \rangle = -\frac{\zeta_\parallel(d) - \gamma_\perp^2 \zeta_\parallel(p)}{(1+\gamma_\perp^2)} = -\zeta_\parallel$$

$$\langle + | u_\xi | 0 \rangle = \langle 0 | u_\xi | - \rangle = -\frac{1}{\sqrt{2}} \frac{\zeta_\perp(d) - \gamma_\parallel \gamma_\perp \zeta_\perp(p)}{(1+\gamma_\perp^2)^{\frac{1}{2}}(1+\gamma_\parallel^2)^{\frac{1}{2}}} = -\frac{}{\sqrt{2}}\zeta_\perp$$

$$\langle + | u_\eta | 0 \rangle = \langle 0 | u_\eta | - \rangle = -\frac{i}{\sqrt{2}} \frac{\zeta_\perp(d) - \gamma_\parallel \gamma_\perp \zeta_\perp(p)}{(1+\gamma_\perp^2)^{\frac{1}{2}}(1+\gamma_\parallel^2)^{\frac{1}{2}}} = \frac{i}{\sqrt{2}}\zeta_\perp \ldots \quad (5)$$

where the spin-orbit coupling coefficients $\zeta_i(d)$ ($\parallel$ and $\perp$ to trigonal axis) are for $3d^8$ configuration and $\zeta_i(p)$ are for $3d^7 4p$ configuration, inclusive of the reduction due to covalency overlap of surrounding s-and p-ligand orbitals and $\gamma_\parallel$ and $\gamma_\perp$ are the $3d^8$ $3d^7$ $4p$ admixtural coefficients associated with the states $|0>$ and $|+>$, $|->$ of eqn.(4), respectively), $\zeta_\parallel$ and $\zeta_\perp$ can then be taken as effective spin-orbit coupling coefficients along and normal to the trigonal axis.

FINE STRUCTURE

The set $|+>, |0>$ and $|->$ behaves as an atomic p-state having $M'_L = 1,0,-1$ respectively so that the appropriate Hamiltonian for the lowest triplet is given by

$$H = V_{trig} - \alpha U_\zeta S_\zeta - \alpha'(U_\xi S_\xi + U_\eta S_\eta) \quad (6)$$

where α, α' are the effective orbital Lande' g-factors (Abragam and Pryce, 1951) $\parallel$ and $\perp$ to the trigonal axis, respectively and takes into account the admixture of the upper levels. Under the trigonal field $^3T_1(P)$ breaks up into π_{xy} (doublet) and π_z (singlet), $^3A_2$ remains unsplit (χ) $^3T_2(F)$ into ψ_{xy} (doublet) and ψ_z (singlet) and the ground triplet $^3T_1(F)$ into ϕ_{xy} (doublet) and ϕ_z (singlet) (Abragram and Pryce 1951). The energy separation of the split components of the ground triplet $^3T_1(F)$ is such that the doublet ϕ_{xy} lies at $-(1/3)\,\Delta$ and the singlet ϕ_z at $(2/3)\Delta$ where Δ is the trigonal field separation. Operating with Hamiltonian (6) over a ^3P term and solving the secular determinant we get the energies as

$$E_0 = \frac{1}{2}\left[\frac{\Delta}{3} + \alpha\zeta_\parallel - S_0\right]$$

$$E_1 = \frac{1}{2}\left[\frac{\Delta}{3} - S_1\right]$$

$$E_2 = -\frac{\Delta}{3} + \alpha\zeta_{\|}$$

$$E_3 = \frac{1}{2}\left[\frac{\Delta}{3} + S_0 + \alpha\zeta_{\|}\right]$$

$$E_4 = \frac{1}{2}\left[\frac{\Delta}{3} + S_1\right] \qquad \ldots (7)$$

$$E_5 = -\frac{\Delta}{3} - \alpha\zeta_{\|}$$

where,

$$S_0 = [(\Delta - \alpha\zeta_{\|})^2 + 8\alpha'^2\zeta_{\perp}^2]^{\frac{1}{2}}$$
$$S_1 = [\Delta^2 + 4\alpha'^2\zeta_{\perp}^2]^{\frac{1}{2}}$$

and the wavefunctions as

$$\phi_0 = a\,|1,-1\rangle + b\,|0,0\rangle + a\,|-1,1\rangle$$
$$\phi_1 = c\,|1,0\rangle + d\,|0,1\rangle$$
$$\phi'_1 = c\,|-1,0\rangle + d\,|0,-1\rangle$$
$$\phi_2 = -\frac{1}{\sqrt{2}}\,|-1,1\rangle + \frac{1}{\sqrt{2}}\,|1,-1\rangle$$
$$\phi_3 = \frac{b}{\sqrt{2}}\,|1,-1\rangle - \sqrt{2}\,a\,|0,0\rangle + \frac{b}{\sqrt{2}}\,|-1,1\rangle \qquad \ldots (8)$$
$$\phi_4 = d\,|1,0\rangle - c\,|0,1\rangle$$
$$\phi'_4 = d\,|-1,0\rangle - c\,|0,-1\rangle$$
$$\phi_5 = |1,1\rangle$$
$$\phi'_5 = |-1,-1\rangle$$

where,

$$a = \frac{2\alpha'\zeta_{\perp}}{\alpha\zeta_{\|} + \Delta + S_0} \cdot b \;; \qquad 2a^2 + b^2 = 1$$

$$d = \frac{2\alpha'\zeta_{\perp}}{\Delta + S_1}\, c \;; \qquad c^2 + d^2 = 1$$

In the above expressions since α and $\zeta_{\|}$ also α' and $\zeta_{\perp}$ appear as products we may replace these by $P_{\|}$ and $P_{\perp}$.

If the trigonal field coefficient Δ is positive the relative positions of the energy levels including the effect of the spin-orbit coupling in ascending order will correspond to the sequence of wave functions ϕ_0, ϕ_2, (ϕ_1, ϕ'_1), (ϕ_5, ϕ'_5) (ϕ_4, ϕ'_4), ϕ_3. For negative value of Δ the arrangement of the wavefunctions in (8) holds good in the order of increasing energy. Since in the former case two non-magnetic singlets ϕ_0 and ϕ_2 come successively, in the two lowermost positions where in the latter case a magnetic doublet (ϕ_1, ϕ'_1) lies immediately above ϕ_0, the effective magnetic moment should be comparatively smaller in the former. Assuming Δ negative to start with and calculating the first and second order magnetic perturbations for only the lowest ϕ_0 and ϕ_1, ϕ'_1 levels, since rest of the levels lie too high above about 1000 cm $^{-1}$, to give appreciable contribution to the susceptibility we get the expression for the mean susceptibility as follows :

$$K = -\frac{N\beta^2}{3k} B\left[\frac{2A^2}{T} + \frac{16B_1^2 k}{D}\left\{ \exp\left(\frac{D}{kT}\right) - 1 \right\}\right]$$

$$+ \frac{N\beta^2}{3} B\left[\left\{ \frac{8(c + \frac{1}{2}\alpha'\kappa_{\perp} d)^2}{E_2 - E_1} + \frac{8\{bc - 2ad + \frac{\alpha'\kappa_{\perp}}{2}(2ac - bd)\}^2}{E_3 - E_1} \right.\right.$$

$$\left. + \frac{4c^2 d^2(\alpha\kappa_{\|} + 2)^2}{E_4 - E_1} + \frac{16(c - \alpha'\kappa_{\perp} d)^2}{E_5 - E_1} \right\}$$

$$\left. + \left\{ \exp\left(\frac{D}{kT}\right) \left(\frac{4a^2(\alpha\kappa_{\|} + 2)^2}{E_2 - E_0} + \frac{16\{(ad - bc) + \frac{\alpha'\kappa_{\perp}}{2}(ac - bd)^2}{E_4 - E_0} \right) \right\} \right]$$

where,

$$A = 2d^2 - \alpha\kappa_{\|} c^2$$

$$B_1 = \left[\left\{ ac + bd - \frac{\alpha'\kappa_{\perp}}{2}(bc + ad) \right\} + \left\{ bc\nu_5 - ac\nu_3 + bd\nu_2 \right\} \right]$$

$$B = \left[2 + \exp\left(\frac{D}{kT}\right) \right]^{-1}$$

$$\kappa_{\|} = \frac{1 - \gamma_{\perp}^2}{1 + \gamma_{\perp}^2} \kappa'_{\|}$$

$$\kappa_{\perp} = \frac{1 - \gamma_{\|}\gamma_{\perp}}{(1 + \gamma_{\perp}^2)^{\frac{1}{2}}(1 + \gamma_{\|}^2)^{\frac{1}{2}}} \cdot \kappa_{\perp}$$

$\kappa_{\|}$ and $\kappa'_{\perp}$ are the actual orbital reduction factors due to covalency, $\kappa_{\|}$ and $\kappa_{\perp}$ can be taken as effective reduction factors inclusive of the effect of $3d^7\ 4p$-admixture. Here again in (9) we can replace $\alpha\kappa_{\|}$ and and $\alpha'\kappa_{\perp}$ by $Q_{\|}$ and $Q_{\perp}$ respectively.

In the expression for B_1 the second term within braces is the contribution from upper π_{xy}, π_z, χ, ψ_{xy} and ψ_z levels coming directly through the lowest level ϕ_0 of (6) calculated similar to Abragam and Pryce (1951) where

$$\nu_2 = \left(\frac{5f^2_2}{24\psi'_{xy}} - \frac{2q^2_2}{\pi'_{xy}} \right) \zeta$$

$$\nu_3 = \left(\frac{2q^2_4}{\pi'_z} + \frac{2q^2_3}{\chi'} \right) \zeta \qquad \ldots \quad (10)$$

$$\nu_5 = \left(\frac{5f_2 f_5}{\sqrt{2}\ \psi'_{xy}} \right) \zeta$$

in which f's are very near to 1 and q's are about 0.1. The denominators in (10) stand for the energy spacing of various states from the ground level. In the absence of the fine structure absorption spectra results we have taken these to be pure cubic field energy spacings. The situation here is formally similar to the octahedrally co-ordinated V^{3+} salts (Bose *et al.*, 1964), where also after the introduction of spin-orbit coupling there is a lowest singlet with a doublet above it. However, in that case D the energy separation between these two lowest levels is less than 10 cm^{-1} and the system behaves as with effective spin = 1, though only $g_{\|}$ value has been observed by paramagnetic resonance method (Zverev and Prokhorov, 1958) since the transition for $g_{\perp}$ can be spanned experimentally only by waves of length $\sim$ 1 mm. In the present case from calculations that follow, (ϕ_1, ϕ'_1) will be appreciably populated at ordinary temperatures and matrix elements corresponding $\left\langle \phi_1 \right| L_\zeta + 2S_\zeta \left| \phi_1 \right\rangle$, $\left\langle \phi'_1 \right| L_\zeta + 2S_\zeta \left| \phi'_1 \right\rangle$, willh ave non-zero values, while the matrix elements for $\left\langle \phi_1 \right| -2S_\xi \left| \phi'_1 \right\rangle$, and $\left| \left\langle \phi_1 \right| L_\eta + 2S_\eta \left| \phi'_1 \right\rangle \right|$ are zero, so that the p.m.r. absorption spectrum corresponding to $g_{\|}$ can be obtained, though with a decreased intensity, while $g_{\perp}$ will be zero. The arrangement of energy levels resembles in some respects that in Cu-acetate where resonance signal comes from a triplet lying $\sim$ 315 cm^{-1} above a non-magnetic singlet (Bleaney and Bowers, 1952) though it must be remembered that in the two cases the mechanisms of the splitting are physically quite different. The expression for g values are as usual

$$g_{\|} = 2[2d^2 - \alpha\kappa_{\|}c^2]$$
$$g_{\perp} = 0 \qquad \ldots \quad (11)$$

but as yet no p.m.r. data are available.

COMPARISION WITH EXPERIMENTAL MEAN SUSCEPTIBILITY AT DIFFERENT TEMPERATURE

While comparing with experimental results we note that $P_{\|}$. $P_{\perp}$, $Q_{\|}$, $Q_{\perp}$ are five adjustable parameters whose values can be decided by fitting with the mean susceptibility at five temperatures (theoretically three since the relative magnitudes of $P_{\|}$, $P_{\perp}$ and $Q_{\|}$ $Q_{\perp}$ are dependent on Δ), if the value of Δ is assumed to remain constant with temperature. However, in view of the large number of earlier experimental findings (Bose *et al.*, 1960, 1961, 1964, 1965) it is very unlikely that Δ should be constant. But since we do not have any anisotropy or resonance data we are not able to find the values of Δ at different temperatures from mean susceptibility, which only was measured for the cubic crystal. On attempting to fit the experimental values on mean susceptibility it is found that no single set of above parameters can bring the fitting within the limits of experimental error at all the temperatures. When the closest approach to one value at a given temperature is made with a given set of parameters the values at other show systematic increasing differences. Since the room temperature experimental mean moment value is always treated as standard we found out the set of the values of the parameters which gave the calculated moment at this temperature very close to the experimental value and also gives nearest approach to the moments at other temperatures. This set of the values of the parameters are $P_{\|} = -240\ \text{cm}^{-1}$, $P_{\perp} = -375\ \text{cm}^{-1}$, $Q_{\|} = .7$, $Q_{\perp} = 1.624$ and $\Delta = -1020\ \text{cm}^{-1}$. Under the present circumstances we are unable to separately calculate α's, k's and ζ's from P's and Q's. $P_{\|}$ and $P_{\perp}$ can further be written as $P_{\|} = \alpha R_{\|}\zeta$ and $P_{\perp} = \alpha' R_{\perp}\ \zeta$, where $\zeta\ (= -325\ \text{cm}^{-1}$: Bose *et al*, 1963) is the free ion spin-orbit coupling coefficient for Ni^{2+} and so $\alpha R_{\|} = 0.74$ and $\alpha' R_{\perp} = 1.15$; R_i ($i = \|$ or $\perp$) is the reduction factor associated with the matrix elements for spin-orbit interaction. These reductions (given by k_i, R_i are due to the anisotropic overlap of the surrounding s-and p-ligand charge clouds with the central d-charge clouds and the admixture of $3d^7\ 4p$ configuration with $3d^8$.

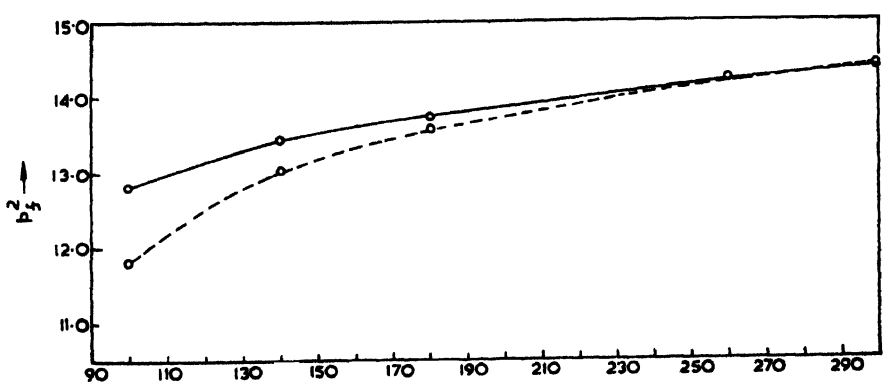

Fig. 1 The full and the dotted curves represent the experimental and thtoretical values respectively.

The systematic increasing difference between the experimental and theoretical results as shown in the table (1.2% at 200°K, ~ 3.1 % at 140°K and ~ 7.0 % at 100°K) gives a clear evidence of the inadequacy of treating the anisotropic parameters as independent of temperature. In particular the parameter Δ might change appreciably from the room temperature value of -1026 cm^{-1} in order to wipe out the 7% disagreement in mean susceptibility at low temperatures, since the mean susceptibility is not very sensitive to the changes of Δ. Of course as Δ changes it is only natural that the relative values of $P_{\|}$, $P_{\perp}$ and $Q_{\|}$, $Q_{\perp}$ will also change correspondingly, thus sharing the task of wiping out the discrepancy between them. This is particularly true for the tetrahedral complexes in which the anisotropic field admixtures and overlaps are comparatively larger than in octahedral complexes and temperature variation of Δ may have greater influence on ($P_{\|}$, $P_{\perp}$) and ($Q_{\|}$, $Q_{\perp}$). This effect, in cases where sufficient experimental data on anisotropy and resonance at different temperatures are available, can be introduced as a *second* approximation, the *first* being the calculation of $P_{\|}$, $P_{\perp}$, $Q_{\|}$ and $Q_{\perp}$ as constant and Δ as the only variable with temperature as done at present.

One interesting point is that the theoretical p_f^2 versus T curve (figure) (considering Δ = constant) shows a rather quicker fall below 200°K($kT \sim 140$ cm^{-1}) owing to the fact that (1) the lowest level ϕ_0 is non-magnetic and (2) the next higher level (ϕ_1, ϕ'_1) is about 150 cm^{-1}. The experimental data above room temperature is not available. But those below show a steady fall of magnetic moment with temperature down to 100°K instead of a sharp fall. Evidently the theoretical sharp fall is counteracted in practice by the appreciable temperature dependence of the anisotropic part of the field. Finally, we considered the case when Δ is

TABLE I

$P_{\|} = -240$ cm^{-1} $\quad P_{\perp} = -375$ cm^{-1}

$Q_{\|} = 0.700$ $\quad Q_{\perp} = 1.624$

$\Delta = -1020$ cm^{-1}

Temperature	Experimental values		Theoretically calculated values	
°K	$\bar{K} \times 10^6$	p_f^2	$\bar{K} \times 10^6$	p_f^2
300	5986	14.36	6008	14.41
260	6840	14.22	6840	14.22
180	9536	13.72	9421	13.56
140	11909	13.33	11643	13.03
100	15997	12.79	14759	11.80

positive. But the mean moment in that case would be very much smaller and practically of the higher frequency type which does not agree with experimental magnetic results.

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